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Surface Chemistry in Electrochemical Atomic Layer Processing

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13. ABSTRACT *(Maximum 200 words)*

Objectives: Atomic layer processing involves the formation and/or etching of materials an atomic layer at a time. Atomic layer epitaxy is the most obvious example, where a thin film of a material is formed an atomic layer at a time. That is, surface limited reactions are used to deposit individual atomic layers of the elements making up a compound. These reactions are used in a cycle, where each cycle results in the formation of a monolayer of the compound. The present studies were designed to investigate these surface limited reactions. To determine what the structures of the deposits were, and how that structure influenced subsequent deposition.

14. SUBJECT TERMS
UPD, ECALE, ALE, electrodeposition, compounds, thin films

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Final Report

1. Project Title: Surface Chemistry in Electrochemical Atomic Layer Processing

2. P.I. John L. Stickney
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3. Grant N00014-91-J-1919, 96Pro-2855, R&T Code 4133036

4. Funding Profile
Total = 832k

Year 1	Year 2	Year 3 (1/2 year)	Year 4	Year 5	Year 6
166K	227k	86K	141K	106K	106K
80k on UHV system	75K on STM		5k XPS software		

5. Objectives: Atomic layer processing involves the formation and/or etching of materials an atomic layer at a time. Atomic layer epitaxy is the most obvious example, where a thin film of a material is formed an atomic layer at a time. That is, surface limited reactions are used to deposit individual atomic layers of the elements making up a compound. These reactions are used in a cycle, where each cycle results in the formation of a monolayer of the compound. The present studies were designed to investigate these surface limited reactions. To determine what the structures of the deposits were, and how that structure influenced subsequent deposition.

6. Published papers resulting from this support

   a. Submitted but not published: 1
   b. Published in refereed journals: 28 (includes accepted and in press)
   c. Published in non refereed journals: 0

7. Number of technical reports submitted: 29

8.Number of books written: 0

9. Number of book chapters: 9

10. Patents as a result of work:
   a. Number filed: 2
   b. Number granted: 2

Brian W. Gregory, Ignacio Villegas, and John L. Stickney "Electrochemical Atomic Layer Epitaxy", U.S. patent, Jun. 14, 1994, #5,320,736.

Paula Lei, Choong Rhee, and John L. Stickney, "Digital Electrochemical Etching of Compound Semiconductors", U.S. patent, Jan. 31, 1995, #5,385,651.

11. Total number of invited presentations: 56

Symposium on "Surface Structure and Electrochemical Reactivity," October 11-15, 1993, Ulm, Germany. This was an invited lecture at a special meeting organized by Professor Kolb. It was the first chance to describe electrochemical ALE to an international

audience. The format was a lot like a GRC.

Symposium on "New Materials for Electrochemistry," Keynote Lecture on "Semiconducting Materials," 45th Meeting of the International Society of Electrochemistry, Porto, Portugal, August 28th - September 2nd, 1994.
This Keynote lecture was presented to the ISE. It covered the first deposits of thin films.

ISE-ECS joint international meeting, Pairs, France, August 31-September 5th, Keynote lecture, symposia on photoelectrochemistry, session on compound semiconductor electrodeposition. This Keynote lecture was to a session on compound semiconductor electrodepositors. It shows our stature in that community that we were selected to speak in that capacity.

13. Number of postdocs supported: 3
    Estimated total person-months: 75

14. Number of graduate students supported: 10
    Estimated number of person months: 150

14.5 Number of undergraduates supported: 8

15. Most significant publications

D.W. Suggs and J.L. Stickney, "Studies of the Surface Structures Formed by the Alternated Electrodeposition of Cd and Te on the Low-Index Planes of Au. Part II: STM Studies," Surface Sci., 290 (1993) 375.

This was the first detailed study of the electrochemical formation of a monolayer of CdTe on a Au single crystal surface using surface analytical methods. LEED, Auger, and STM were used to determine the structures of the first monolayers on each of the low index planes of Au.

T.A. Sorenson, B.K. Wilmer, J.L. Stickney, "Electrochemical Digital Etching: Atomic Level Studies of CdTe(100)," American Chemical Society Symposium Series, 656, Solid-Liquid Electrochemical Interfaces, 656(1996)115.

This is the paper where electrochemical digital etching was examined at the atomic level. Studies where reported where atomic layers of Cd and Te were alternately removed from a single crystal of CdTe. The concept of underpotential etching was also introduced to account for the loss of more Te then would have otherwise been expected.

J.L. Stickney "Electrochemical Atomic Layer Epitaxy," in "Electroanalytical Chemistry," Ed. A.J. Bard, Marcel Dekker, New York accepted.

This is a comprehensive review of the work that has been performed under the support for this grant. It covers the literature, including a table with over 400 references. It includes descriptions of studies with thin layer electrodes, automated flow cell deposition, atomic level surface studies, digital electrochemical etching, and suggested future directions.

15. Major Accomplishments:

This funding has allowed the concept of electrochemical atomic layer epitaxy (ALE) to be made a reality. Films have been grown, electrochemical ALE does work.

An atomic level picture of the formation of the first monolayers of a compound have been studied. This is one of the most complete studies of its kind, and the only one of its kind for the electrochemical process.

We have developed an automated electrochemical flow deposition system which can be programmed to deposit a number of different compounds, including CdTe, CdSe, CdS, and ZnS.

An electrochemical form of digital etching has been invented and patented.

The nature of atomic layers of chalcogenides have been investigated and characterized. Excellent control over the coverages was obtained by use of electrochemical deposition.

Se eight membered rings were discover on Au(111) and Au(100). The growth and phase transitions between chains, dimers and trimers of chalcogenides on the where observed and investigated.

17. Transitions:

Investigations of the deposition of CdS by electrochemical ALE on InP crystals. Work performed at the request of Kenneth Vaccaro, USAF Rome Laboratory, RL/EROC, 80 Scott Road, Hanscom AFB, MA 01731-2909. CdS films 30 nm thick where deposited on InP(100) substrates.

18. Summery of the overall impact of work in this period.

These studies have served to change the way electrochemists view the electrodeposition of compounds. Instead of forming a compound by taking a solution and dipping in a electrode and plating what you can, there is now the option of taking the compound deposition process and decomposing it into a series of steps. Each can be studied individually, and optimized. It is significantly more realistic now to think of how high quality epitaxial electrodeposited thin films could be formed. This is becoming an international concern. There are groups in England and Italy that we know about that are actively pursuing programs in electrochemical ALE. We have produced high quality films this summer that we feel will elicit much increased interest in the area, but are just now being written up. A very solid basis has been laid for electrochemical ALE, as a result of this funding, it is just a mater of refining the deposition process and producing examples of devices that can be studied and compared with existing structures.

19. Electrodeposition, ECALE, UPD, compounds